

## Supplementary Information

### **Tracking intramolecular energy redistribution dynamics in aryl halides: The effect of halide mass**

Xiaosong Liu,<sup>a</sup> Yunfei Song,<sup>b†</sup> Wei Zhang,<sup>a</sup> Gangbei Zhu,<sup>b</sup> Zhe Lv,<sup>a</sup> Weilong Liu,<sup>a</sup> and Yanqiang Yang<sup>a,b,\*</sup>

<sup>a</sup> Department of Physics, Harbin Institute of Technology, Harbin, China

<sup>b</sup> National Key Laboratory of Shock Wave and Detonation Physics, Institute of Fluid Physics, China Academy of Engineering Physics, Mianyang, China

Molecule	Peak	Frequencies of coupling modes /cm <sup>-1</sup>	Beat frequency/cm <sup>-1</sup>
F-Ph	Q <sub>1</sub>	3072 and 2373	701
	Q <sub>2</sub>	3084 and 2373	711
	Q <sub>3</sub>	3072 and 2525	547
	Q <sub>4</sub>	3084 and 2525	559
Cl-Ph	Q <sub>1</sub>	3052 and 2257	795
	Q <sub>2</sub>	3067 and 2257	810
	Q <sub>3</sub>	3052 and 2511	541
	Q <sub>4</sub>	3067 and 2511	556
	Q <sub>5</sub>	2257 and 2511	254
Br-Ph	Q <sub>1</sub>	3056 and 2229	827
	Q <sub>2</sub>	3065 and 2229	836
	Q <sub>3</sub>	3056 and 2509	547
	Q <sub>4</sub>	3065 and 2509	556
	Q <sub>5</sub>	2229 and 2509	280
I-Ph	Q <sub>1</sub>	3048 and 2216	832
	Q <sub>2</sub>	3070 and 2216	854
	Q <sub>3</sub>	3048 and 2504	544
	Q <sub>4</sub>	3070 and 2504	566
	Q <sub>5</sub>	2216 and 2504	288

Table 1. Frequency differences between high frequency C-H stretching modes and combination bands of aryl halides. Vibrational energy flow from red-coded parent modes to blue-coded daughter modes and beat frequencies between parent modes and daughter modes are signed

Molecule	peak	Frequencies of coupling modes /cm <sup>-1</sup>	Beat frequency/cm <sup>-1</sup>
F-Ph	Q <sub>1</sub>	1457 and 1603	146
	Q <sub>2</sub>	1496 and 1596	100
	Q <sub>3</sub>	1496 and 1603	107
Cl-Ph	Q <sub>1</sub>	1443 and 1583	140
	Q <sub>2</sub>	1479 and 1583	104
	Q <sub>3</sub>	1443 and 1479	36
Br-Ph	Q <sub>1</sub>	1577 and 1263	314
	Q <sub>2</sub>	1319 and 1577	258
	Q <sub>3</sub>	1441 and 1263	178
	Q <sub>4</sub>	1441 and 1577	136
	Q <sub>5</sub>	1472 and 1577	105
	Q <sub>6</sub>	1441 and 1472	31
I-Ph	Q <sub>1</sub>	1469 and 1255	214
	Q <sub>2</sub>	1436 and 1255	181
	Q <sub>3</sub>	1436 and 1441	130
	Q <sub>4</sub>	1318 and 1436	118
	Q <sub>5</sub>	1469 and 1571	102
	Q <sub>6</sub>	1436 and 1469	33

Table 2. Frequency differences between the C-C stretching modes and in-plane C-H deformations of aryl halides. Vibrational energy flow from red-coded parent modes to blue-coded daughter modes and beat frequencies between parent modes and daughter modes are signed

Molecule	Peak	Frequencies of coupling modes /cm <sup>-1</sup>	Beat frequency/cm <sup>-1</sup>
F-Ph	Q <sub>1</sub>	1010 and 1155	144
	Q <sub>2</sub>	1010 and 1218	203
	Q <sub>3</sub>	1024 and 1218	194
	Q <sub>4</sub>	1457 and 1596	142
	Q <sub>5</sub>	1496 and 1596	101
	Q <sub>6</sub>	1496 and 1603	107
Cl-Ph	Q <sub>1</sub>	1068 and 1443	374
	Q <sub>2</sub>	1002 and 1322	326
	Q <sub>3</sub>	965 and 1174	217
	Q <sub>4</sub>	987 and 1157	177
	Q <sub>5</sub>	1002 and 1157	148
	Q <sub>6</sub>	1002 and 1083	77
	Q <sub>7</sub>	1024 and 1068	40
	Q <sub>8</sub>	1479 and 1583	96
	Q <sub>9</sub>	1443 and 1479	33
Br-Ph	Q <sub>1</sub>	1158 and 990	168
	Q <sub>2</sub>	1020 and 1158	143
	Q <sub>3</sub>	1071 and 963	100
	Q <sub>4</sub>	1001 and 1068	69
	Q <sub>5</sub>	1020 and 1001	27
	Q <sub>6</sub>	1176 and 1441	270
	Q <sub>7</sub>	1263 and 1441	74
	Q <sub>8</sub>	1319 and 1577	147
	Q <sub>9</sub>	1263 and 1319	59
	Q <sub>10</sub>	1441 and 1472	31
I-Ph	Q <sub>1</sub>	1156 and 1571	406
	Q <sub>2</sub>	1068 and 1436	368
	Q <sub>3</sub>	1156 and 1469	315
	Q <sub>4</sub>	1156 and 1436	283
	Q <sub>5</sub>	1175 and 1436	252
	Q <sub>6</sub>	1156 and 1318	172
	Q <sub>7</sub>	999 and 1156	159
	Q <sub>8</sub>	1175 and 1318	140
	Q <sub>9</sub>	1318 and 1436	117
	Q <sub>10</sub>	1175 and 1255	83
	Q <sub>11</sub>	1017 and 1060	36

Table 3. Frequency differences between vibrational modes from 900 to 1600cm<sup>-1</sup> of aryl halides. Vibrational energy flow from red-coded parent modes to blue-coded daughter modes and beat frequencies between parent modes and daughter modes are signed

Molecule	Peak	Frequencies of coupling modes /cm <sup>-1</sup>	Beat frequency/cm <sup>-1</sup>
F-Ph	Q <sub>1</sub>	1218 and 900	318
	Q <sub>2</sub>	1155 and 900	255
	Q <sub>3</sub>	982 and 759	223
	Q <sub>4</sub>	1010 and 831	179
	Q <sub>5</sub>	1010 and 1155	145
	Q <sub>6</sub>	955 and 807	148
	Q <sub>7</sub>	1010 and 900	110
	Q <sub>8</sub>	807 and 900	93
	Q <sub>9</sub>	759 and 807	48
	Q <sub>10</sub>	1010 and 1068	58
Cl-Ph	Q <sub>1</sub>	1024 and 741	283
	Q <sub>2</sub>	1068 and 832	236
	Q <sub>3</sub>	682 and 902	220
	Q <sub>4</sub>	1002 and 902	100
	Q <sub>5</sub>	702 and 832	132
	Q <sub>6</sub>	1002 and 1083	81
	Q <sub>7</sub>	1024 and 1068	44
Br-Ph	Q <sub>1</sub>	1020 and 673	347
	Q <sub>2</sub>	1001 and 673	328
	Q <sub>3</sub>	681 and 906	225
	Q <sub>4</sub>	737 and 906	169
	Q <sub>5</sub>	990 and 906	84
	Q <sub>6</sub>	1020 and 1068	48
	Q <sub>7</sub>	1020 and 1071	51
	Q <sub>8</sub>	1158 and 1176	18
I-Ph	Q <sub>1</sub>	1255 and 904	321
	Q <sub>2</sub>	1175 and 904	271
	Q <sub>3</sub>	1068 and 1255	187
	Q <sub>4</sub>	988 and 1156	168
	Q <sub>5</sub>	654 and 838	184
	Q <sub>6</sub>	1017 and 1156	139
	Q <sub>7</sub>	1060 and 1175	115
	Q <sub>8</sub>	1175 and 1255	80
	Q <sub>9</sub>	999 and 1060	61
	Q <sub>10</sub>	684 and 731	47

Table 4. Frequency differences between vibrational modes from 650 to 1200cm<sup>-1</sup> of aryl halides. Vibrational energy flow from red-coded parent modes to blue-coded daughter modes and beat frequencies between parent modes and daughter modes are signed

$B_2$ , 224	$B_1$ , 396	$A_2$ , 401	$B_2$ , 498	$A_1$ , 521	$B_1$ , $\alpha_{CCC}$ ,614
$B_2$ , $\phi_{CC}$ ,675	$B_2$ , $\gamma_{CH}$ ,750	$A_1$ , $\nu_{CF}^2$ , 867	$A_2$ , $\gamma_{CH}$ ,802	$B_2$ , $\gamma_{CH}$ ,913	$A_2$ , $\gamma_{CH}$ ,891
$B_2$ , $\gamma_{CH}$ ,955	$A_1$ , $\nu_{CCH}$ ,974	$A_1$ , $\beta_{CH}$ ,997	$B_1$ , $\beta_{CH}$ ,1067	$A_1$ , $\delta_{CCH}$ ,1150	$B_1$ , $\beta_{CH}$ ,1155
$A_1$ , $\nu_{CF}^1$ ,1209	$B_1$ , $\beta_{CH}$ ,1298	$B_1$ , $\nu_{CC}$ ,1317	$B_1$ , $\nu_{CC}$ ,1455	$A_1$ , $\nu_{CC}$ ,1491	$A_1$ , $\nu_{CC}$ ,1601
$B_1$ , $\nu_{CC}$ ,1610	$A_1$ , $\nu_{CH}$ ,3107	$B_1$ , $\nu_{CH}$ ,3116	$A_1$ , $\nu_{CH}$ ,3128	$B_1$ , $\nu_{CH}$ ,3136,	$A_1$ , $\nu_{CH}$ ,3137

Table 5. Vibrational symmetry type and vibrational structure of fluorobenzene(F-Ph), the nonharmonic vibrational frequencies of those normal modes are computed by density functional theory (DFT) with a Becke-Lee-Yang-Parr function (B3LYP) and the 6-311G basis set, as implemented in the Gaussian 03 computational package. Frequency units are  $\text{cm}^{-1}$

B <sub>2</sub> , 183	B <sub>1</sub> , 292	A <sub>1</sub> , $\phi_{CC}$ ,405	A <sub>2</sub> , 407	B <sub>2</sub> , 471	B <sub>1</sub> , $\alpha_{CCC}$ ,614
B <sub>2</sub> , $\phi_{CC}$ ,690	A <sub>1</sub> , $\nu_{CCl^2}$ ,694	B <sub>2</sub> , $\gamma_{CH}$ ,741	A <sub>2</sub> , $\gamma_{CH}$ ,823	B <sub>2</sub> , $\gamma_{CH}$ ,901	A <sub>2</sub> , $\gamma_{CH}$ ,961
B <sub>2</sub> , $\gamma_{CH}$ ,983	A <sub>1</sub> , $\nu_{CCH}$ ,994	A <sub>1</sub> , $\delta_{CCH}$ ,1020	B <sub>1</sub> , $\beta_{CH}$ ,1073	A <sub>1</sub> , $\nu_{CCl^1}$ ,1074	B <sub>1</sub> , $\beta_{CH}$ ,1157
A <sub>1</sub> , $\beta_{CH}$ ,1172	B <sub>1</sub> , $\beta_{CH}$ ,1291	B <sub>1</sub> , $\nu_{CC}$ ,1314	B <sub>1</sub> , $\nu_{CC}$ ,1446	A <sub>1</sub> , $\nu_{CC}$ ,1471	A <sub>1</sub> , $\nu_{CC}$ ,1588
B <sub>1</sub> , $\nu_{CC}$ ,1591	A <sub>1</sub> , $\nu_{CH}$ ,3107	B <sub>1</sub> , $\nu_{CH}$ ,3114	A <sub>1</sub> , $\nu_{CH}$ ,3127	B <sub>1</sub> , $\nu_{CH}$ ,3138	A <sub>1</sub> , $\nu_{CH}$ ,3140

Table 6. Vibrational symmetry type and vibrational structure of chlorobenzene(Cl-Ph), the nonharmonic vibrational frequencies of those normal modes are computed by density functional theory (DFT) with a Becke-Lee-Yang-Parr function (B3LYP) and the 6-311G basis set, as implemented in the Gaussian 03 computational package. Frequency units are cm<sup>-1</sup>

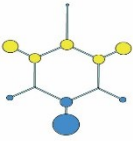
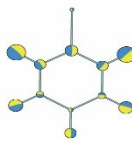
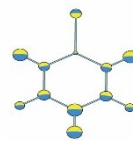
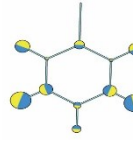
B <sub>2</sub> ,163	B <sub>1</sub> ,245	A <sub>1</sub> ,306	A <sub>2</sub> , $\phi_{CC}$ ,405	B <sub>2</sub> ,457	B <sub>1</sub> , $\alpha_{CCC}$ ,614
					
A <sub>1</sub> , $\nu_{CBr^2}$ ,666	B <sub>2</sub> , $\phi_{CC}$ ,683	B <sub>2</sub> , $\gamma_{CH}$ ,732	A <sub>2</sub> , $\gamma_{CH}$ ,825	B <sub>2</sub> , $\gamma_{CH}$ ,900	A <sub>2</sub> , $\gamma_{CH}$ ,961
B <sub>2</sub> , $\gamma_{CH}$ ,983	A <sub>1</sub> , $\nu_{CCH}$ ,993	A <sub>1</sub> , $\delta_{CCH}$ ,1015	A <sub>1</sub> , $\nu_{CBr^1}$ ,1059	B <sub>1</sub> , $\beta_{CH}$ ,1073	B <sub>1</sub> , $\beta_{CH}$ ,1159
					
A <sub>1</sub> , $\beta_{CH}$ ,1175	B <sub>1</sub> , $\beta_{CH}$ ,1289	B <sub>1</sub> , $\nu_{CC}$ ,1314	B <sub>1</sub> , $\nu_{CC}$ ,1442	A <sub>1</sub> , $\nu_{CC}$ ,1473	A <sub>1</sub> , $\nu_{CC}$ ,1582
B <sub>1</sub> , $\nu_{CC}$ ,1590	A <sub>1</sub> , $\nu_{CH}$ ,3105	B <sub>1</sub> , $\nu_{CH}$ ,3113	A <sub>1</sub> , $\nu_{CH}$ ,3126	B <sub>1</sub> , $\nu_{CH}$ ,3137	A <sub>1</sub> , $\nu_{CH}$ ,3139

Table 7. Vibrational symmetry type and vibrational structure of bromobenzene(Br-Ph), the nonharmonic vibrational frequencies of those normal modes are computed by density functional theory (DFT) with a Becke-Lee-Yang-Parr function (B3LYP) and the 6-311G basis set, as implemented in the Gaussian 03 computational package. Frequency units are cm<sup>-1</sup>



B <sub>2</sub> ,158	B <sub>1</sub> ,220	A <sub>1</sub> ,266	A <sub>2</sub> , $\phi_{CC}$ ,398	B <sub>2</sub> ,450	B <sub>1</sub> , $\alpha_{CCC}$ ,613
A <sub>1</sub> , $\nu_{Cl^2}$ ,654	B <sub>2</sub> , $\phi_{CC}$ ,680	B <sub>2</sub> , $\gamma_{CH}$ ,728	A <sub>2</sub> , $\gamma_{CH}$ ,818	B <sub>2</sub> , $\gamma_{CH}$ ,890	A <sub>2</sub> , $\gamma_{CH}$ ,958
B <sub>2</sub> , $\gamma_{CH}$ ,978	A <sub>1</sub> , $\nu_{CCH}$ ,979	A <sub>1</sub> , $\delta_{CCH}$ ,1011	A <sub>1</sub> , $\nu_{Cl^1}$ ,1052	B <sub>1</sub> , $\beta_{CH}$ ,1068	B <sub>1</sub> , $\beta_{CH}$ ,1152
A <sub>1</sub> , $\beta_{CH}$ ,1171	B <sub>1</sub> , $\beta_{CH}$ ,1255	B <sub>1</sub> , $\nu_{CC}$ ,1311	B <sub>1</sub> , $\nu_{CC}$ ,1436	A <sub>1</sub> , $\nu_{CC}$ ,1469	A <sub>1</sub> , $\nu_{CC}$ ,1571
B <sub>1</sub> , $\nu_{CC}$ ,1571	A <sub>1</sub> , $\nu_{CH}$ ,3090	B <sub>1</sub> , $\nu_{CH}$ ,3099	A <sub>1</sub> , $\nu_{CH}$ ,3101	B <sub>1</sub> , $\nu_{CH}$ ,3128	A <sub>1</sub> , $\nu_{CH}$ ,3130

Table 8. Vibrational symmetry type and vibrational structure of iodobenzene (I-Ph), the nonharmonic vibrational frequencies of those normal modes are computed by the Moller-Plesset Perturbation Method (MP2) with the AUG-cc-pVTZ basis set on C, H atoms, and the AUG-cc-pVTZ-pp basis set on I atom, as implemented in the Gaussian 03 computational package. Frequency units are cm<sup>-1</sup>